PREPARATION OF SYNTHETIC POLYMER FROM PLASTIC WASTE USING SULPHUR DIOXIDE

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ABSTRACT

The synthesis of polymer using sulphur dioxide gas is being studied in this research. The objective of this research is to obtain a new synthetic polymer that contains hydrophilic property. This research also contributes towards sustaining the green environment because we recycle the waste. High density polyethylene (HDPE) polymer and sulphur dioxide gas were used in this research. The reaction between HDPE and sulphur dioxide will yield a new synthetic polymer that contains hydrophilic property and biodegradable. The functional group of the product which is sulfonic acid was identified by using Fourier Transform Infrared spectrometer (FTIR). The synthetic polymer might be a potentially valuable source as a fabric, for the usage of chemical feed stocks and also material for membrane technology.

ABSTRAK

Sintesis polimer dengan menggunakan gas sulfur dioksida sedang dipelajari dalam kajian ini. Tujuan kajian ini adalah untuk mendapatkan polimer sintetik baru yang mempunyai ciri-ciri hidrofilik. Kajian ini juga memberikan sumbangan dalam pemeliharaan persekitaran hijau kerana kami mengitar semula sampah. Polimer polietilena ketumpatan tinggi (HDPE) dan gas sulfur dioksida digunakan dalam kajian ini. Reaksi antara HDPE dan gas sulphur dioksida akan menghasilkan polimer sintetik baru yang mempunyai cirri-ciri hidrofilik dan biodegredasi. Kumpulan berfungsi dari produk yang dikenalpasti dengan menggunakan Fourier Transform spektrometer Inframerah (FTIR) adalah kumpulan asid sulfonik. Polimer sintetik boleh menjadi sumber yang berharga berpotensi sebagai kain, penggunaan bahan mentah kimia dan juga bahan untuk teknologi membran.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

HDPE	-	High density polyethylene
kg	-	gram
^0C	-	degree Celsius
Pa	-	Pressure (Pascal)
m^3	-	Metre cubic
FTIR	-	Fourier transform infrared spectroscopic
FKKSA	-	Faculty of Chemical Engineering and Natural Resources

LIST OF APENDICES

CHAPTER 1

INTRODUCTION

1.1 Introduction

During last decades, the great population increase worldwide with the need of the people to adopt improved conditions of living led to a dramatically increase of the consumption of polymers (mainly plastics).Materials that appears to interwoven with the consuming society where we live. (D.S Achilias, 2008)

Current statistics for Malaysia estimate the annual total consumption of plastic products at 1.4 million tons for 2003. This total exceeded the 1.1 million tones annual consumption preceding the 1997 financial crisis.(Malaysian Plastics Manufacturers Association, MPMA, 2005)

In Malaysia we produce 19,000 tonnes of waste every day, and a majority of that ends up in landfills. Malaysia currently has 230 landfill sights and 80% of them will reach capacity within the next two years, and with land for landfill sites being at a premium there is soon going to be a big problem right on our doorsteps. To put in perspective 19,000 tonnes of rubbish,; if you piled it all up it would be as high as 36 Petronas Twin Towers, that’s an awful lot of rubbish to deal with on a daily basis.

1.2 Plastic Waste

Polyolefin (LDPE, HDPE, PP) are a major type of thermoplastics used throughout the world in such applications as bags, toys, containers, pipes (LDPE), house wares, industrial wrappings and film, gas pipes (HDPE), film, battery cases, automotive parts, electric components (PP). These years have also shown significant developments in rational polymer synthesis. (D.S Achilias, 2008)

Most commercially important polymers today are entirely synthetic and produced in high volume on appropriately scaled organic synthetic techniques. Synthetic polymers today find application in nearly every industry and area of life. Polymers are widely used as adhesives and lubricants, as well as structural components for products ranging from children's toys to aircraft. (Painter P. C. and Coleman M. M., 2006)

They have been employed in a variety of biomedical applications ranging from implantable devices to controlled drug delivery. Polymers such as poly(methyl methacrylate) find application as photo resist materials used in semiconductor manufacturing and low-k dielectrics for use in high-performance microprocessors. Recently, polymers have also been employed as flexible substrates in the development of organic light-emitting diodes for electronic displays. (Painter P. C. and Coleman M. M., 2006)

1.3 Problem Statement

Plastic does not decompose easily. If burnt, plastic waste emits toxic fumes. Current methods of treating plastic waste in Malaysia include incineration, land fill disposal and recycling. In many industrialized countries, landfill space is dwindling. Plastic waste disposal is also becoming an increasingly costly affair such as the cost of automated sorting machines. This has made recycling an urgent exercise.

Recycling also has it consequences such as the high level of contamination in the household plastics. Besides that, plastics are lightweight and it is expensive to pick up and sort. Virgin resins are cheaper to buy and some resins are difficult to be cleaned.

Concern for the environment in these countries has led to demands for safer methods of disposal. Incineration, in the last five years, it is estimated that our consumption of plastic has increased by more than 10 per cent. Recycling is now not just an environmental issue but a necessity. Plastic recycling in this country is still in its infancy.

1.4 Objectives of Research

The objective of this research is to:-

i) Obtain a new synthetic polymer that contains hydrophilic property.

ii) Experiment the polymerization using sulphur dioxide.

iii) Characterize the synthetic polymer

1.5 Scope of Work

On this research, there are focuses on two main scopes:

i. Recycling

   a. High density polyethylene (HDPE) is dissolved in non polar solvent, reacted with sulphur dioxide gas and precipitated with polar solvent to form polymer resin

ii. Characteristic

a. Fourier Transform Infra Red (FTIR) is used to determine the polymer's hydrophilic characteristic.

1.6 Rationale and Significance

The rationale of this research is the polymer that will not decompose in nature can be reduced by recycling the polymers such as plastic bags. Recycling also helps in saving a lot of space that usually gets wasted while making landfills for waste. Also, we can conserve natural resources for our future generations. So, get into the habit of recycling things so that they can be reused and therefore, a lot of energy and money can be saved.

CHAPTER 2

LITERATURE REVIEW

2.1 Background of Synthetic Polymer

Starting in 1811, Henri Braconnot did pioneering work in derivative cellulose compounds, perhaps the earliest important work in polymer science. The development of vulcanization later in the nineteenth century improved the durability of the natural polymer rubber, signifying the first popularized semi-synthetic polymer. In 1907, Leo Baekeland created the first completely synthetic polymer, Bakelite, by reacting phenol and formaldehyde at precisely controlled temperature and pressure. Bakelite was then publicly introduced in 1909. (Sperling L.H, 2006)

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Despite significant advances in synthesis and characterization of polymers, a correct understanding of polymer molecular structure did not emerge until the 1920s. Before then, scientists believed that polymers were clusters of small molecules (called colloids), without definite molecular weights, held together by an unknown force, a concept known as association theory. In 1922, Hermann Staudinger proposed that polymers consisted of long chains of atoms held together by covalent bonds, an idea which did not gain wide acceptance for over a decade and for which Staudinger was ultimately awarded the Nobel Prize. (Sperling L.H, 2006)

The Work by Wallace Carothers in the 1920s also demonstrated that polymers could be synthesized rationally from their constituent monomers. An important contribution to synthetic polymer science was made by the Italian chemist Giulio Natta and the German chemist Karl Ziegler, who won the Nobel Prize in Chemistry

in 1963 for the development of the Ziegler-Natta catalyst. (Sperling L.H, 2006)

Further recognition of the importance of polymers came with the award of the Nobel Prize in Chemistry in 1974 to Paul Flory, whose extensive work on polymers included the kinetics of step-growth polymerization and of addition polymerization, chain transfer, excluded volume, the Flory-Huggins solution theory, and the Flory convention. (Sperling L.H, 2006)

2.2 Polymer Properties

Polymer properties are broadly divided into several classes based on the scale at which the property is defined as well as upon its physical basis. The most basic property of a polymer is the identity of its constituent monomers. A second set of properties, known as microstructure, essentially describe the arrangement of these monomers within the polymer at the scale of a single chain. These basic structural properties play a major role in determining bulk physical properties of the polymer, which describe how the polymer behaves as a continuous macroscopic material. Chemical properties, at the nano-scale, describe how the chains interact through various physical forces. At the macro-scale, they describe how the bulk polymer interacts with other chemicals and solvents. (Rubinstein, M. and Colby, R., 2006)

2.2.1 Monomers

The identity of the monomer residues (repeat units) comprising a polymer is its first and most important attribute. Polymer nomenclature is generally based upon the type of monomer residues comprising the polymer. Polymers that contain only a single type of repeat unit are known as photopolymers, while polymers containing a mixture of repeat units are known as copolymers. Poly(styrene), for example, is composed only of styrene monomer residues, and is therefore classified as a

photopolymer. Ethylene-vinyl acetate, on the other hand, contains more than one variety of repeat units and is thus a copolymer. Some biological polymers are composed of a variety of different but structurally related monomer residues; for example, polynucleotides such as DNA are composed of a variety of nucleotide subunits. (Rubinstein, M. and Colby, R., 2006)

2.2.2 Microstructure

The microstructure of a polymer (sometimes called configuration) relates to the physical arrangement of monomer residues along the backbone of the chain. These are the elements of polymer structure that require the breaking of a covalent bond in order to change. Structure has a strong influence on the other properties of a polymer. For example, two samples of natural rubber may exhibit different durability, even though their molecules comprise the same monomers. (Sperling L.H, 2006)

2.2.3 Polymer Architecture

An important micro structural feature determining polymer properties is the polymer architecture. The simplest polymer architecture is a linear chain: a single backbone with no branches. A related unbranching architecture is a ring polymer. A branched polymer molecule is composed of a main chain with one or more substituent side chains or branches. Special types of branched polymers include star polymers, comb polymers, brush polymers, ladders, and dendrimers. (Rubinstein, M. and Colby, R., 2006)

Branching of polymer chains affects the ability of chains to slide past one another by altering intermolecular forces, in turn affecting bulk physical polymer properties. Long chain branches may increase polymer strength, toughness, and the glass transition temperature due to an increase in the number of entanglements per chain. The effect of such long-chain branches on the size of the polymer in solution

is characterized by the branching index. Random length and atactic short chains, on the other hand, may reduce polymer strength due to disruption of organization and may likewise reduce the crystallinity of the polymer.

A good example of this effect is related to the range of physical attributes of polyethylene. High-density polyethylene (HDPE) has a very low degree of branching, is quite stiff, and is used in applications such as milk jugs. Low-density polyethylene (LDPE), on the other hand, has significant numbers of both long and short branches, is quite flexible, and is used in applications such as plastic films.

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Dendrimers are a special case of polymer where every monomer unit is branched. This tends to reduce intermolecular chain entanglement and crystallization. Alternatively, dendritic polymers are not perfectly branched but share similar properties to dendrimers due to their high degree of branching.

The architecture of the polymer is often physically determined by the functionality of the monomers from which it is formed. This property of a monomer is defined as the number of reaction sites at which may form chemical covalent bonds. The basic functionality required for forming even a linear chain is two bonding sites. Higher functionality yields branched or even cross linked or networked polymer chains. (Campbell, Neil A.; Brad Williamson; Robin J. Heyden, 2006)

An effect related to branching is chemical cross linking - the formation of covalent bonds between chains. Cross linking tends to increase Tg and increase strength and toughness. Among other applications, this process is used to strengthen rubbers in a process known as vulcanization, which is based on cross linking by sulphur. Car tires, for example, are highly cross linked in order to reduce the leaking of air out of the tire and to toughen their durability. Eraser rubber, on the other hand, is not cross linked to allow flaking of the rubber and prevent damage to the paper.

A cross-link suggests a branch point from which four or more distinct chains

emanate. A polymer molecule with a high degree of cross linking is referred to as a polymer network. Sufficiently high crosslink concentrations may lead to the formation of an infinite network, also known as a gel, in which networks of chains are of unlimited extent — essentially all chains have linked into one molecule. (Painter, P and Coleman, M., 2006)

2.2.4 Chain Length

The physical properties of a polymer are strongly dependent on the size or length of the polymer chain. For example, as chain length is increased, melting and boiling temperatures increase quickly. (Rubinstein, M. and Colby, R., 2006)

Impact resistance also tends to increase with chain length, as does the viscosity, or resistance to flow, of the polymer in its melt state. Chain length is related to melt viscosity roughly as 1:103.2, so that a tenfold increase in polymer chain length results in a viscosity increase of over 1000 times. Increasing chain length furthermore tends to decrease chain mobility, increase strength and toughness, and increase the glass transition temperature (Tg). (McCrum, N. G., Buckley, C. P., and Bucknall, C. B., 1997)

This is a result of the increase in chain interactions such as Van der Waals attractions and entanglements that come with increased chain length. These interactions tend to fix the individual chains more strongly in position and resist deformations and matrix breakup, both at higher stresses and higher temperatures. (McCrum, N. G., Buckley, C. P., and Bucknall, C. B., 1997)

A common means of expressing the length of a chain is the degree of polymerization, which quantifies the number of monomers incorporated into the chain. (McCrum, N. G., Buckley, C. P., and Bucknall, C. B., 1997), (Rubinstein, M. and Colby, R., 2006) As with other molecules, a polymer's size may also be expressed in terms of molecular weight. Since synthetic polymerization techniques

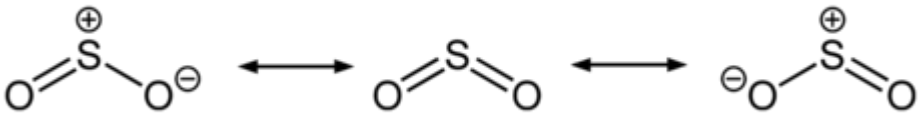
typically yield a polymer product including a range of molecular weights, the weight is often expressed statistically to describe the distribution of chain lengths present in the same. Common examples are the number average molecular weight and weight average molecular weight. (McCrum, N. G., Buckley, C. P., and Bucknall, C. B., 1997), (Rubinstein, M. and Colby, R., 2006)

The ratio of these two values is the polydispersity index, commonly used to express the "width" of the molecular weight distribution. (Painter P. C. and Coleman M. M., 1997) A final measurement is contour length, which can be understood as the length of the chain backbone in its fully extended state. (Rubinstein, M. and Colby, R., 2003) The flexibility of an unbranched chain polymer is characterized by its persistence length.

2.3 Polymerization

Polymerization is the process of combining many small molecules known as monomers into a covalently bonded chain. During the polymerization process, some chemical groups may be lost from each monomer. This is the case, for example, in the polymerization of PET polyester. The monomers are terephthalic acid (HOOC-C6H4-COOH) and ethylene glycol (HO-CH2-CH2-OH) but the repeating unit is -OC-C6H4-COO-CH2-CH2-O-, which corresponds to the combination of the two monomers with the loss of two water molecules. The distinct piece of each monomer that is incorporated into the polymer is known as a repeat unit or monomer residue.

Sulphur dioxide is used for polymerization because of its role as good reducing and oxidising agent. . In terms of electron-counting formalisms, the sulphur atom has an oxidation state of +4, a formal charge of 0, and is surrounded by 5 electron pairs and can be described as a hypervalent molecule. From the perspective of molecular orbital theory, most of these valence electrons are engaged in S–O bonding.



Three resonance structures of sulphur dioxide

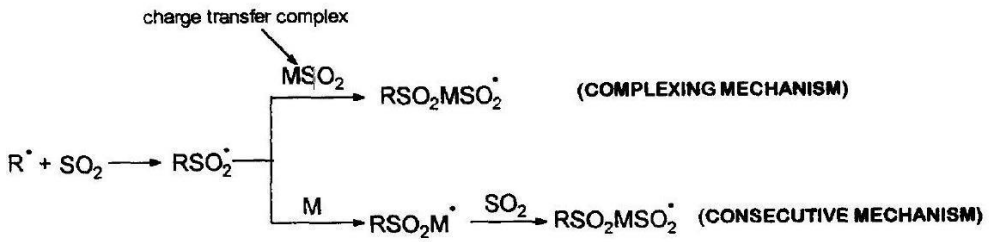
In free radical polymerization, sulphur dioxide role is been categorized into two: that is sulphur dioxide as monomer and sulphur dioxide as initiator

2.3.1 Sulphur Dioxide as Monomer

The free radical polymerization of vinyl monomers and some alkynes in sulphur dioxide normally results in the incorporation of sulphur dioxide into the polymer backbone. Generally, the formed polysulfones can be classified into two categories: linear alternating copolymers,-(-M-SO,-),-, and polysulfones with variable compositions. (Golubev, V.B, 1994)

Linear alternating copolymers are obtained by the reaction of sulfur dioxide and electron donor monomers of low resonance stabilization in the growing chain. These monomers include aliphatic olefins, 1-alkynes, some dienes, and ally1 alcohol and vinyl acetate, among others. Two alternatives have been proposed, as described in Scheme 7. (Golubev, V.B, 1994)

The first possibility suggests the formation of charge-transfer complexes between the olefin (electron donor) and sulfur dioxide (electron acceptor). The donor-acceptor complex may perform as a new monomer itself. Thus, the copolymerization process may be considered as a homopolymerization of the co-monomer complex (“complexing mechanism”). The other possibility involves a consecutive addition of monomers (“consecutive mechanism”).



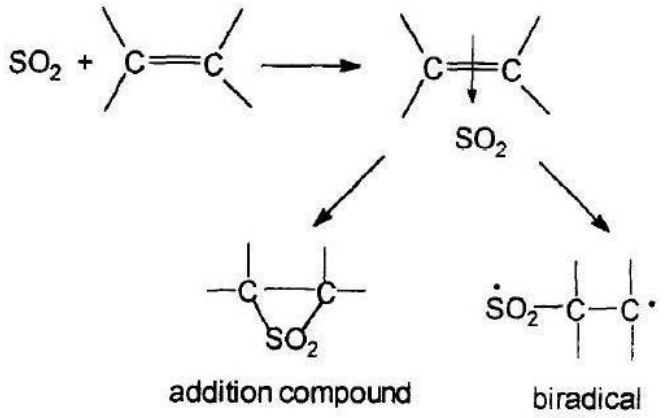
Scheme 7. Scheme proposed by Golubev for the of alternating copolymerization.

2.3.2 Sulphur Dioxide as Initiator

. Sulphur dioxide in very low concentrations (catalytic concentrations) can also act as an initiator for the free radical polymerizations of vinyl compounds at ambient temperatures. (Ghosh, P. and O'Driscoll, K. F., 1966)

The polymerization of methyl methacrylate in methanol (1: 1 ~01%) initiated by SO_2 gives rise to 100% of conversion after 10 days of reaction at 30°C. Styrene polymerizes more slowly, resulting in a 50% conversion after 30 days of reaction. The polymerization of MMA was accelerated by using basic solvents. The following order of polymerizability was found for different solvents: pyridine > dimethylformamide (DMF) > dimethyl sulfoxide (DMSO > methanol > benzene. The polymerization still proceeds in the presence of air and is not inhibited. (Ghosh, P. and O'Driscoll, K. F., 1966)

The induction period is lower in photo-polymerization than under thermal conditions and decreases with higher SO_2 concentrations. The SO_2-induced photo-polymerization was inhibited by hydroquinone and air, suggesting that a free radical mechanism was operating. '32 It was suggested that SO_2 forms a complex with the C=C double bond of MMA and this charge-transfer complex is responsible for the initiation. Thus, the radical generation step may involve bi-radical formation which is accelerated by photo-activation.



Scheme 9. Mechanism proposed by Ghosh and Chakraborty for initiation in photopolymerizations initiated by sulfur dioxide.

2.4 Polymer Recycling

Disposing of the waste to landfill is becoming undesirable due to legislation pressures (waste to landfill must be reduced by 35% over the period from 1995 to 2020), rising costs and the poor biodegradability of commonly used polymers.

The approaches that have been proposed for recycling of waste polymers include (Scheirs, 1998; Achilias and Karayannidis, 2004): *Primary Recycling* referring to the "in-plant" recycles of the scrap material controlled history.

Mechanical Recycling, where the polymer is separated from its associated contaminants and it is reprocessed by melt extrusion. *Chemical Recycling* leading in total depolymerization to the monomers, or partial degradation to other secondary valuable materials.

Energy recovery is an effective way to reduce the volume of organic materials by incineration. Among the recycling techniques, incineration meets with strong societal opposition and mechanical recycling can be carried out only on single-polymer waste streams.

However, the most attractive method, in accordance also with the principles of sustainable development is chemical recycling also called as feedstock or tertiary recycling. According to this method waste polymer can be either converted to original monomers or other valuable chemicals. These products are useful as feedstock for a variety of downstream industrial processes or as transportation fuel.

2.5 Sources of Plastic Waste

Industrial waste (or primary waste) can often be obtained from the large plastics processing, manufacturing and packaging industries. Rejected or waste material usually has good characteristics for recycling and will be clean. Although the quantity of material available is sometimes small, the quantities tend to be growing as consumption, and therefore production, increases.

Commercial waste is often available from workshops, craftsmen, shops, supermarkets and wholesalers. A lot of the plastics available from these sources will be PE, often contaminated. Agricultural waste can be obtained from farms and nursery gardens outside the urban areas. This is usually in the form of packaging (plastic containers or sheets) or construction materials (irrigation or hosepipes).

Municipal waste can be collected from residential areas (domestic or household waste), streets, parks, collection depots and waste dumps. In Asian cities this type of waste is common and can either be collected from the streets or can be collected from households by arrangement with the householders. (Lardinois, 1995)

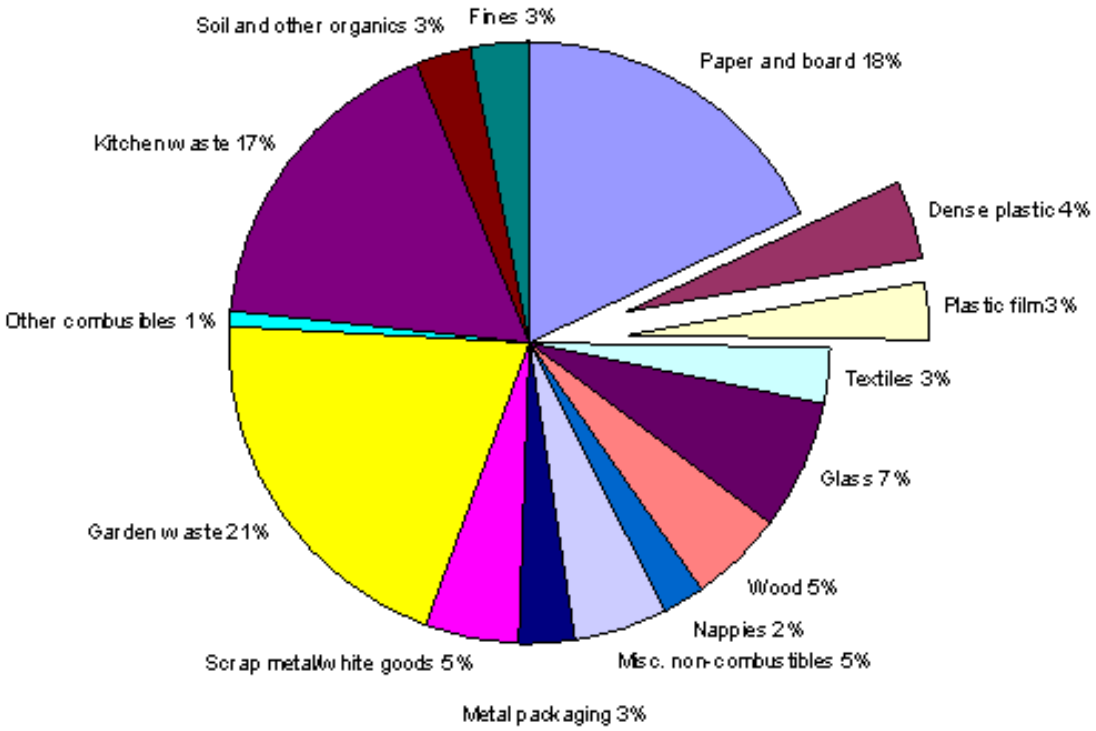


Figure 2.1: Household Waste Compositions (Dr. J. Parfitt, WRAP, December 2002)

CHAPTER 3

METHODOLOGY

3.1 Materials

The main material is high density polyethylene (HDPE) with density between 910 and 985 kg/m^3. Sulphur dioxide gas with 99% purity was purchased from Linde Industrial Gas Malaysia through FKKSA Lab Technical Unit. Reagent grade n-hexane with 98.5 % by weight and reagent grade xylene with 82 % by weight were purchased through FKKSA Lab Technical Unit.

3.2 Experiment Set Up and Method

Before set up this experiment, design of the reactor was made up from Quartz glass reaction vessel with diameter 6 inches x 8 inch height that were fabricated. This is to ensure the reactor can withstand high temperature and high pressure. Operating condition: The reaction takes place at 140^{o}C. Flow rate of the gas supplied into the reactor controlled by flow meter and the pressure is monitored with a pressure gauge. The source water for the condenser is tap water. The design of the polymer synthesis system was shown in Figure 3.1.